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(54) N-(ω-AMINOALKANE)-ω′-AMINOALKANE SULPHONIC ACID SALTS AND THEIR USE AS ANIONIC STRUCTURAL COMPONENTS IN THE PREPARATION OF EMULSIFIER-FREE POLYURETHANE DISPERSIONS

(71) We, BAYER AKTIENGESELLSCHAFT formerly Farbenfabriken Bayer Aktiengesellschaft a body corporate organised under the laws of Germany of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to N - (ω - aminoalkane) - ω′ - aminoalkane sulphonic acid salts and their use as anionic structural components in the preparation of emulsifier-free polyurethane dispersions.

Aminosulphonic acids may be used *inter alia* as intermediate products for the production and modification of synthetic resins and for the production of detergents. In particular diaminosulphonic acids, e.g. 2,4-diaminobenzene-sulphonic acid and their salts are suitable for use as anionic structural components in the preparation of polyurethane dispersions which are free from emulsifiers (Belgian Patent Specification No. 673,432).

These aromatic diaminosulphonic acids, which are readily accessible, are mostly commercially available products but are usually only moderately soluble in the solvents commonly used. Furthermore they make the polyurethanes made from them very sensitive to light and liable to yellow. Polyurethane dispersions produced from these aromatic diamino-sulphonic acids undergo discoloration on exposure to light, and coatings, films and foils produced from these dispersions are not fast to light.

The problem therefore existed of finding a reproducible method of preparing light-fast polyurethane dispersions from diaminosulphonic acids which would be economical, physiologically innocous, and which would result in a product which could be obtained in a high degree of purity on a commercial scale.

Although processes for the preparation of aliphatic diaminosulphonic acids whose salts are suitable for use as anionic structural components for light-fast polyurethane dispersions are already known, these known processes either entail considerable expenditure in apparatus or involve the use of physiologically very dangerous starting materials e.g. (reaction of sultone with amines).

It has now been found that aliphatic diamino sulphonic acid salts of Formula II may be obtained under simple reaction conditions by reacting compounds of Formula I with aliphatic di-primary diamines as follows:

$$NH_2—(CH_2)_n—NH_2 + HO—(CH_2)_m—SO_3M \rightarrow$$
I

$$N_2H(CH_2)_n—NH—(CH_2)_m—SO_3M$$ II

wherein M=sodium, potassium, lithium, rubidium, caesium or an unsubstituted or substituted ammonium cation and n=2—12, preferably 2, 3, 4, or 6 and m=1—6, preferably 1, 2, 3 or 4.

This invention therefore provides a process for the preparation of N - (ω - aminoalkane) - ω′ - aminoalkanesulphonic acid salts of the formula

$$NH_2—(CH_2)_n—NH—(CH_2)_m—SO_3^-M^+$$

in which

M^+ is an alkali metal cation or a substituted or unsubstituted ammonium cation,

n is an integer from 2 to 12 and

m is an integer from 1 to 6,

in which a compound of the formula

$$HO—(CH_2)_m—SO_3^-M^+$$

is reacted with an aliphatic diamine of the formula

$$NH_2—(CH_2)_n—NH_2$$

This invention also relates to N - (ω - aminoalkane) - ω′ - aminoalkanesulphonic acid salts of the formula

$$NH_2—(CH_2)_n—NH—(CH_2)_m—SO_3^-M^+$$

in which n is an integer from 2 to 12, m is 1 or 2 and M^+ represents an alkali metal cation or an unsubstituted or substituted ammonium cation, preferably sodium or potassium.

Lastly, this invention also provides a process for the preparation of aqueous polyurethane dispersions which are emulsifier-free which comprises reacting an isocyanate prepolymer with a N - (ω - aminoalkane - ω′ - aminoalkane sulphonic acid salt according to the invention and then adding water.

The reaction of hydroxyalkane sulphonic acid salts with monoamines is already known. Surprisingly, it has been found that polyamines, and particularly aliphatic diprimary amines, may also be reacted with hydroxysulphonic acid salts without side reactions, so that no unwanted by-products are formed.

The diaminosulphonic acid salts according to the invention are immediately ready for use without purification and may be used directly for the preparation of anionic emulsifier-free polyurethane dispersions.

The following are given as examples of amines of the formula

$$NH_2—(CH_2)_n—NH_2$$

ethylene diamine, propylene - 1,3 - diamine, butylene - 1,4 - diamine, hexamethylene - 1, 6 - diamine, octamethylene - 1,8 - diamine, decamethylene - 1,10 - diamine and dodecamethylene - 1,12 - diamine.

The following are given as examples of compounds of Formula I which may be used as starting materials for the preparation of the new compounds: The salts, e.g. sodium, potassium or triethylammonium salts of hydroxymethane - sulphonic acid, of β - hydroxy - ethanesulphonic acid, of δ-hydroxybutane sulphonic acid or of ω - hydroxyhexane - sulphonic acid.

It is preferred to use the salts of the first two acids mentioned for the process according to the invention.

The reaction may be carried out in polar solvents which are inert under the conditions of the reaction, e.g. dimethylsulphoxide or dimethylformamide, preferably using substantially stoichiometric quantities of the reactants or an excess of diamine, but it may also be mixing the starting materials together, in which case the diamine is preferably used in stoichiometric excess.

The reaction temperature is preferably between 100 and 300°C, in particular between 150 and 250°C. If desired, the reaction may be carried out at pressures above atmospheric in an autoclave.

The molar ratio to compound I put into the reaction should preferably be at least 1:1. If a higher ratio is used, the excess amine remaining after the reaction may be removed, e.g. by distillation, or it may be left in the reaction mixture without it interfering in subsequent processes carried out with the reaction mixture.

The new compounds are intermediate products for the production and modification of synthetic resins. The products which are particularly suitable for the production of anionic polyurethane dispersions which are free from emulsifiers are the N - (β - aminoethyl) - β - aminoethanesulphonic acid salts produced by the process of the invention, and especially sodium - N - (β - aminoethyl) - β - aminoethanesulphonate prepared by the condensation of sodium β - hydroxyethanesulphonate with ethylene diamine.

Dispersions of salts of the N - (ω - amino-

alkane) - ω' - aminoalkanesulphonic acids may also be prepared very economically, and lightfast and colourless films, foils, threads, coatings, impregnations, bonds and intermediate layers can be produced from these dispersions.

For the preparation of aqueous emulsifier-free polyurethane dispersions, a prepolymer containing isocyanate groups is advantageously first prepared from a high molceular weight polyhydroxyl compound preferably having a molecular weight of up to 20,000 and more preferably from 600 to 4000, at least one polyisocyanate and if desired at least one low molecular weight chain lengthening agent which contains reactive hydrogen atoms, and this prepolymer is then reacted in the form of a solution, preferably in an organic solvent, with the N - (ω - aminoalkane) - ω' - aminoalkanesulphonic acid salt used according to the invention, which may also be in the form of a solution before being mixed with the solution of the isocyanate prepolymer. The resulting high molecular weight, anionic polyurethanes, which are predominantly linear or branched, are extracted into the aqueous phase by the addition of water, and the organic solvent is preferably completely or partly removed at the same time or subsequently. (As is customary in the polyurethane are the term "high molecular weight" as applied to polyols means having a molecular weight above 300 whilst "low molecular weight" means a molecular weight below 300).

In principle, the said aqueous polyurethane dispersions could also be prepared by stirring the prepolymer which contains isocyanate groups into the N - (ω - aminoalkane) - ω' - aminoalkane - sulphonic acid salt which has been introduced into a reaction vessel.

Alternatively, all the water together with the N - (ω - aminoalkane) - ω' - aminoalkanesulphonic acid salt may be added to the isocyanate-containing prepolymer.

As starting material for the preparation of the dispersions there may be used e.g. the higher molecular weight polyhydroxyl compounds having a molecular weight of 300 to 20,000 mentioned in French Patent Specification No. 1,416,564 and in Belgian Patent Specification No. 673,432, polyisocyanates and chain lengthening agents which contain reactive hydrogen atoms.

The higher molecular weight polyhydroxyl compounds used are mainly linear compounds having a molecular weight of about 300 to 20,000 preferably 600 to 4000. Hydroxyl-containing polyesters, polyacetals, polyacetones, polycarbonates, polyethers and polyester amides are preferred. The hydroxyl number of these compounds is generally 10 to 100 and preferably 50 to 70. The chain lengthening agents with reactive hydrogen atoms may be glycols, diamines, amino alcohols or water. These compounds may, if desired, be used together with the higher molecular weight polyhydroxyl compounds, these lower molecular weight compounds having molecular weights of up to 300. Alternatively, the process may be carried out without these low molecular weight compounds.

In order to vary the resistance to water, the handle, the surface character and gloss of the impregnations, coats, films and bonds obtained from the products of the process, it is in many cases advantageous if the higher molecular weight polyhydroxyl compounds consist partly or entirely of carbofunctional polysiloxanes which contain reactive hydroxyl groups and which have a molecular weight of 300 to 20,000, preferably 600 to 4000.

Carbofunctional polysiloxanes of this type and their preparation have been described, for example, in French Patent Specification No. 1,291,937, in German Auslegeschrift No. 1,114,632 and U.K. Patent Nos. 1,128,642 and 1,176,490.

The polyisocyanates used may be any aromatic or aliphatic or cycloaliphatic, diisocyanates, and for the production of polyurethanes masses which do not undergo discoloration in light it is especially suitable to use aliphatic or cyclo-aliphatic diisocyanates e.g. butane - 1,4 - diisocyanate, hexane - 1,6 - diisocyanate, isophorone diisocyanate, diisocyanatocarboxylic acid esters e.g. the ethyl ester of 2,6 - diisocyanatohexanoic acid, trimethylhexanediioscyanate, dicyclohexylmethanediisocyanate, cyclohexane - 1,4 - diisocyanate, 1 - methyl - cyclohexane - 2,4 - and - 2,6 - diisocyanate and mixtures thereof. Phenylene - 1,3 - diisocyanate and - 1,4 - diisocyanate, xylylenediisocyanate, tolylene - 2,4 - diisocyanate and - 2,6 - diisocyanate and 4,4 - diisocyanate - diphenylmethane are given as examples of suitable aromatic diisocyanates.

The solvents used for the prepolymer which contains iocyanate group are preferably low boiling organic solvents, e.g. acetone, tetrahydrofuran, methylethylketone or tertiary butane diol, but low boiling solvents which are immiscible with water, e.g. benzene or methylene chloride, may also be used.

The solvents used for the diaminosulphonic acid salt may be low boiling alcohols e.g. methanol or ethanol or water, if desired with the addition of other organic solvents.

As a rule, the prepolymer which contains isocyanate groups is preferably prepared at elevated temperatures, those of between 110 and 130°C being employed when aliphatic diisocyanates are used. For aromatic diisocyanates, temperatures of from 60 to 100°C are generally sufficient. For the preparation of the prepolymer, the quantity of polyisocyanate is advantageously chosen so that all the groups which are capable of reacting with isocyanate groups will undergo reaction;

a slight excess of diisocyanates over and above this amount may be used. The ratio of isocyanate groups to the groups which are reactive with isocyanate groups is generally not greater than 1.3 to 1.5.

When the melt has cooled, the prepolymer is taken up in the organic solvent, and the N - ω - (ω - aminoalkane) - ω' - aminoalkane - sulphonic acid salt is then added at 20 to 80°C, if desired in the form of a solution. If unduly high viscosities occur in the preparation of the prepolymer, solvents e.g. acetone, tetrahydrofuran or methyl ethyl ketone may be added and pressures above atmospheric may be used to prevent solvent loss.

The proportion of sulphonate groups $SO_3(-)$ in the polyurethane is generally from 0.5 to 7% by weight, preferably 0.5 to 4% by weight. The quantities of N - (ω - aminoalkane) - ω' - aminoalkane - sulphonic acid salts should be chosen accordingly. The sulphonate group content may thus be varied within wide limits but should not fall below the aforesaid limit because otherwise the stability of the dispersions which according to the invention are prepared without the use of auxiliary agents e.g. emulsifiers, dispersing agents or swelling agents, would be impaired.

To bring the polyurethanes into the aqueous phase, the organic solvent may be removed by distillation or by blowing air or gas through the solution to remove the solvent, e.g. at temperatures of between 30 and 80°C. Removal of the solvent is preferably carried out by evaporation under vacuum.

In this way, aqueous dispersions can be obtained in the form of non-sedimenting latices which vary from low viscosity to high viscosity products and which have an average particle size of between 0.02 and 1.0 μ, preferably 0.05 to 0.2 μ, and a solids content of generally 20 to 60% by weight.

Dispersions generally dry directly at room temperature or elevated temperatures to form dimensionally stable foils or coatings. It is preferred to employ elevated temperatures for drying. The dispersions according to the invention may subsequently be cross-linked, e.g. by means of polyfunctional cross-linking substances e.g. formaldehyde, or compounds which liberate formaldehyde or like formaldehyde will produce cross-linking, e.g. hexamethylolmeamine or carbamic acid resins, phenol resins, masked polyisocyanates or polyepoxides. Cross-linked coatings, impregnated materials and bonding layers are then obtained.

Dispersions according to the invention are used mainly as coatings and impregnating agents for various substrates e.g. paper, cardboard, textiles, leather, fleeces, wood and metals and as bonding agents, binders and adhesives and for the production of threads, films and foils. The moulded articles, coatings and impregnated materials obtained from the dispersions are distinguished by their high resistance to water and oil and they compare particularly favourably with products which have been produced e.g. from 2,4 - diaminobenzenesulphonic acid in accordance with Belgian Patent Specification No. 673,432 in being colourless and lightfast as required.

The dispersions may be blended with anionic polymer or copolymer dispersions, for example polymer or copolymer dispersions of vinyl chloride, ethylene, styrene, butadiene, vinylidene chloride, vinyl acetate, acrylates and acrylonitrie. Wetting agents, dispersing agents, stabilizers, fillers, plasticizers, pigments, carbon black, aluminium and dispersions of clay, asbestos or tar may also be incorporated with the dispersions.

The following Examples illustrate the invention:—

Example 1

296 g of sodium - β - hydroxyethanesulphonate and 360 g of 100% ethylenediamine are heated to 190°C at 5.5 atmospheres gauge for 6 hours under autogenous pressure, and excess ethylenediamine and the water of reaction are then distilled off under vacuum. The resulting sodium salt of N - (β - aminoethyl) - β - aminoethanesulphonic acid is diluted to a 50% by weight solution with 360 g of water and is used in this form as anionic component for the preparation of emulsifier-free polyurethane dispersions. Yield: 360 g of salt=95% of the theory.

Example 2

246 g of potassium hydroxyethanesulphonate and 522 g of hexamethylenediamine are heated to 200°C under an autogenous pressure of 4 atmospheres gauge for 6 hours, and excess hexamethylenediamine and the water of reaction are then distilled off under vacuum.

The resulting potassium salt of N - β - (ω - aminohexyl) - ω' - aminoethanesulphonic acid is diluted to a 50% by weight solution with 402 g of water and used in this form as anionic component for the preparation of emulsifier-free polyurethane dispersions. Yield: 402 g of salt=95% of the theory.

Example 3

250 g of a polyester of adipic acid/ethylene glycol (OH number 56) are dehydrated for 30 minutes at 120°C and then reacted with 40 g of hexane - 1,6 - dissocyanate at 120° C for 2 hours. This prepolymer, which contains isocyanate groups, is cooled to 55°C and taken up in 700 ml of acetone. 23.8 g of the 50% by weight solution of sodium N - (β - aminoethyl) - β - aminoethane

sulphonate (prepared according to Example 1) in 100 ml of water are added to this acetone-containing prepolymer solution with rapid stirring. 450 ml of water are then stirred in. The reaction mixture is then stirred again until the streakiness which at first appears has disappeared and the reaction mixture has become homogeneous. The acetone is distilled off under vacuum (water pump) at 55°C. The resulting dispersion has a solids content of 40.3% by weight and a residual acetone content of 0.6% by weight. It dries at room temperature to form clear, colourless foils which have high elasticity and tensile strength.

Example 4

425 g of a polyester of adipic acid, hexane - 1,6 - diol and neopentylglycol (molar ratio 30:22:12; OH number 67) are dehydrated at 120°C for 30 minutes and then reacted with 76 g of hexane - 1,6 - diisocyanate at 120°C. The prepolymer, which contains isocyanate groups, is cooled and taken up in 1500 ml of acetone. 65.0 g of the 50% by weight solution of potassium N - (ω - aminohexyl) - β -aminoethanesulphonate (prepared according to Example 2) in 100 ml of water are added to this prepolymer solution. After briefly stirring the reaction mixture again 650 ml of water are added and the acetone is evaporated off under vacuum. The resulting dispersion has a solids content of 42.9% by weight and dries to form clear, colourless foils which have a high tensile strength.

Example 5

The procedure is the same as in Example 3 but 250 g of polypropylene glycol ether (OH number 56) are used instead of the polyester, and 36 g of tolylene diisocyanate (2,4 - and 2,6 - isomer mixture, ratio of isomers 65:35) are used instead of hexane - 1,6 - diisocyanate and the prepolymer reaction is carried out at 80°C instead of at 120°C. A stable dispersion having a solids content of 39% by weight is obtained which dries to form a soft, slightly sticky film.

WHAT WE CLAIM IS:—

1. A process for the preparation of N - (ω - aminoalkane) - ω' - aminoalkanesulphonic acid salts of the formula

$$NH_2—(CH_2)_n—NH—(CH_2)_m—SO_3^-M^+$$

in which

M^+ is an alkali metal cation or a substituted or unsubstituted ammonium cation,

n is an integer from 2 to 12

and

m is an integer from 1 to 6,

in which a compound of the formula

$$HO—(CH_2)_m—SO_3^-M^+$$

is reacted with an aliphatic diamine of the formula

$$NH_2—(CH_2)_n—NH_2$$

2. A process as claimed in Claim 1 in which M^+ is sodium or potassium.

3. A process as claimed in Claim 1 or Claim 2 in which the hydroxy sulphonate salt used is a salt of hydroxymethane sulphonic acid or β - hydroxy - ethane sulphonic acid.

4. A process as claimed in any of claims 1 to 3 which is carried out in a polar solvent inert under the conditions of the reaction.

5. A process as claimed in any of claims 1 to 4 which is carried out at a temperature between 100°C and 300°C.

6. A process as claimed in Claim 5 which is carried out at a temperature between 150° C and 250°C.

7. A process as claimed in any of claims 1 to 6 in which substantially stoichiometric amounts of the sulphonate salt and diamine are used.

8. A process as Claim 1 substantially as herein described with reference to Examples 1 or 2.

9. A sulphonate salt of the formula

$$NH_2—(CH_2)_n—NH—(CH_2)_m—SO_3^-M^+$$

in which

M^+ is an alkali metal cation or a substituted or unsubstituted ammonium

n is an integer from 2 to 12

and

m is 1 or 2.

10. A salt as claimed in Claim 9 in which n is 2, 3, 4 or 6.

11. A salt as claimed in Claim 9, the preparation of which is described in one of the Examples 1 or 2.

12. A process for the preparation of an emulsifier free aqueous polyurethane dispersion which comprises reacting an isocyanate prepolymer wtih a sulphonate salt as claimed in any one of Claims 9 to 11 and then adding water.

13. A process as claimed in Claim 12 in which a solution of the isocyanate prepolymer in an organic solvent is reacted with the sulphonate salt and water is then added.

14. A process as claimed in Claim 13 in which the sulphonate salt is also in solution before being mixed with the solution of the isocyanate prepolymer.

15. A process as claimed in claim 13 or claim 14 in which any organic solvent present in the dispersion after the addition of water, is removed.

16. A process as claimed in claim 12 in which the sulphonate salt and water are added to the isocyanate prepolymer.

17. A process as claimed in any of claims 12 to 16 in which the isocyanate prepolymer has been prepared from

(a) at least one high molecular weight (as herein defined polyhydroxyl compound and
(b) at least one polyisocyanate.

18. A process as claimed in claim 17 in which the high molecular weight polyhydroxyl compound has a molecular weight of up to 20,000.

19. A process as claimed in claim 18 in which the molecular weight of the polyhydroxyl compound is from 600 to 4,000.

20. A process as claimed in any of claims 17 to 19 in which the prepolymer has been prepared using, in addition, at least one low molecular weight (as herein defined) chain lengthening agent which comprises reactive hydrogen atoms.

21. A process as claimed in any of claims 12 to 19 in which the polyurethane produced comprises 0.5 to 7% by weight of sulphonate groups.

22. A process as claimed in claim 21 in which the polyurethane comprises 0.5 to 4% by weight of sulphonate groups.

23. A process as claimed in claim 12 substantially as herein described with reference to any one of the Examples 3 to 5.

24. Emulsifier-free aqueous polyurethane dispersions when produced by a process as claimed in any of Claims 12 to 23.

25. Foils of coatings produced by drying a dispersion as claimed in cliam 24.

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